

Switchable ErSc₂N rotor within a C₈₀ fullerene cage: An EPR and photoluminescence excitation study

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Systems exhibiting both spin and orbital degrees of freedom, of which Er³⁺ is one, can offer mechanisms for manipulating and measuring spin states via optical excitations. Motivated by the possibility of observing photoluminescence and electron paramagnetic resonance from the same species located within a fullerene molecule, we initiated an EPR study of Er³⁺ in ErSc₂N@C₈₀. Two orientations of the ErSc₂N rotor within the C₈₀ fullerene are observed in EPR, consistent with earlier studies using photoluminescence excitation (PLE) spectroscopy. For some crystal field orientations, electron spin relaxation is driven by an Orbach process via the first excited electronic state of the ⁴I_{15/2} multiplet. We observe a change in the relative populations of the two ErSc₂N configurations upon the application of 532 nm illuminations, and are thus able to switch the majority cage symmetry. This photoisomerisation, observable by both EPR and PLE, is metastable, lasting many hours at 20 K.

Photoswitchable structural phenomena are essential to many natural processes. In the laboratory, they have been observed in a wide range of organic [1] and inorganic [2] species, with switching times as short as a picosecond [3]. Natural photoisomerisation (such as bleaching of rod and cone retinal pigments in sight [4]) has been exploited to engineer optical switches which can be used to store information [5] and stimulate neurons [6]. Fullerenes have been shown to provide remarkable nanovoids in which atoms, ions and molecules can exhibit nearly-free behaviour within a solid state environment. Examples include the quantised rotational states in C₂Sc₂@C₈₄ [7] and the exceptionally narrow electron paramagnetic resonance (EPR) lines of atomic nitrogen in N@C₆₀ [8]. It is common for such “endohedral” fullerenes to possess several stable structural isomers, though no evidence of photoisomerisation in such systems has thus far been reported.

Although neither the fullerene C₈₀ nor the trimetallic nitride species Er_xSc_{3-x}N ($x=0-3$) is known to exist in isolation, the incarceration of such species within the fullerene cage results in the stable structure Er_xSc_{3-x}N@C₈₀, where the four-atom planar unit sits in the center of the cage [9]. There are a number of configurations of the ErSc₂N rotor within the cage, as determined by X-ray crystallography and photoluminescence (PL) spectroscopy [10, 11].

In this letter, we report the EPR signature of Er³⁺ within ErSc₂N@C₈₀, making this the first endohedral ion known to be directly excitable both by EPR and optical techniques [12, 13]. The EPR spectra indicate two primary configurations with considerable axial g anisotropy. The temperature dependence of the linewidths are consistent with an Orbach mechanism via a higher electronic state of the Er³⁺ ion, allowing us to assign the EPR peaks to configurations measured in PL. In addition, we report

the photoisomerisation of the configuration of ErSc₂N encapsulated within a C₈₀ cage. We find that there are two primary configurations of the ErSc₂N unit, whose populations may be manipulated by optical excitation: an excess of one configuration, obtained by thermal annealing, is converted into an excess of the other under illumination.

ErSc₂N@C₈₀ was purchased from Luna Innovations, and was further purified using high performance liquid chromatography (HPLC). The sample, containing $\sim 10^{15}$ ErSc₂N@C₈₀ molecules dissolved in toluene, was freeze-pumped in liquid nitrogen for five cycles to deoxygenate the solvent and was sealed under vacuum in a quartz EPR tube. CW EPR experiments were performed using an X-band Bruker EMX Micro EPR spectrometer equipped with a rectangular TE₁₀₂ resonator (with optical access) and a low temperature helium-flow Oxford ESR900 cryostat. Measurements were performed in the temperature range 5 – 30 K. A Nd:YAG laser was used to provide 532 nm illumination with a power of about 15 mW. Photoluminescence excitation (PLE) spectra at 5 K on frozen CS₂ solution were acquired using an InGaAs array detector (Princeton Instruments) mounted on a Spex 1877B triple spectrometer. A laser diode, tunable between 1420 and 1520 nm, was used for the excitation at a power of 18 mW.

Charge transfer across the molecule results in the nominal ionic configuration Er³⁺(Sc³⁺)₂N³⁻@C₈₀⁶⁻. The Er³⁺ ion is commonly used in doped glasses and crystals to generate optical amplification media [14] and has been studied extensively using EPR in a variety of hosts [15, 16, 17, 18, 19, 20]. It is known to fluoresce in the near-infrared regime due to the allowed optical transitions between the ground state ⁴I_{15/2} and first excited state ⁴I_{13/2}. Photoluminescence spectroscopy reveals that the ground state of Er³⁺ in this system is split

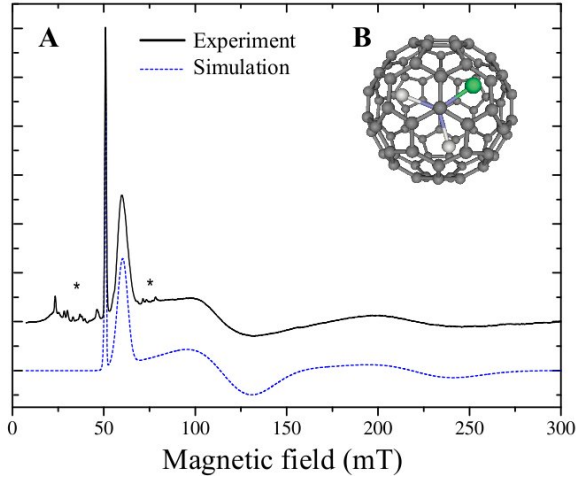


FIG. 1: (A) X-band CW EPR spectrum of $\text{ErSc}_2\text{N}@C_{80}$ in frozen toluene solution at 5 K, with accompanying simulation performed using EasySpin [23]. The low-intensity sharp features marked * derive mostly from hyperfine coupling to the ^{167}Er nuclear spin (natural abundance 22.9 %). Experimental parameters: microwave frequency, 9.396 GHz; microwave power, 63 mW; modulation amplitude, 0.3 mT; modulation frequency, 100 kHz. B) A representation of the $\text{ErSc}_2\text{N}@C_{80}$ molecule.

into eight Kramers doublets, which can then be further split by an external magnetic field [21, 22]. Extensive mixing of m_J within these states enables the observation of EPR between the doublets, which are traditionally treated as pseudo-spin 1/2 systems with a large effective g factor [15].

The CW EPR spectrum of $\text{ErSc}_2\text{N}@C_{80}$ in frozen toluene solution at 5 K shown in Figure 1. The widths of the two most intense features (at ~ 51 and 60 mT) are plotted as a function of temperature in Figure 2. Assuming that the features are homogeneously broadened and that the transverse relaxation time T_2 is limited only by the spin-lattice relaxation time T_1 then the width $\delta\omega$ is proportional to T_1^{-1} . A common mechanism for T_1 relaxation in such systems with low-lying excited states is the two-phonon Orbach process [24], for which

$$\delta\omega \propto T_1^{-1} \propto (e^{\Delta/k_B T} - 1)^{-1} + \text{const.}, \quad (1)$$

where Δ represents the energy of the excited state which forms the relaxation pathway. The close correlation between Δ (obtained from fits to Equation 1 shown as solid lines in Figure 2) and the energy of the first excited state as determined by PL [11] suggests that these two features in the EPR spectrum are associated with the two principal configurations of ErSc_2N within the fullerene cage. In order to explain the full EPR spectrum we similarly assign the broader features at higher field, though their weak intensity at 5 K makes the analogous temperature study more challenging.

Photoluminescence (PL) measurements demonstrate

that the fullerene cage (and, as a result, the Er^{3+} ion) can be excited at 532 nm. Figure 3 shows the effect of such illumination on the CW EPR spectrum of $\text{ErSc}_2\text{N}@C_{80}$. The intensities of the principal features of the spectrum show a marked dependence on illumination: those centred at ~ 51 and 220 mT decrease in intensity, while those at about ~ 60 and 110 mT increase. This confirms that the high-field features have the same origin as the sharper low-field features, and indicates which pairs correspond to each of the primary configurations (which we term here *Conf 1* and *Conf 2*). The CW spectrum in Figure 1 should therefore be modelled with two independent contributions, each generating one low-field feature and one broader high-field feature; and the relative intensities of the contributions reflect the relative populations of *Conf 1* and *Conf 2* configurations (see below).

Differences in the crystal field and spin-orbit coupling for the Er^{3+} ions in the two configurations produce two different effective spin systems. Although each is strictly a high spin system with a large crystal field splitting, only the ground state doublet is occupied at the temperatures studied here; the effective spin may be conveniently represented by an $S=1/2$ spin with an effective g tensor. The dashed line in Figure 1 shows a simulation of the powder spectrum of a two such spin systems: $g_{\perp} = 3.0$, $g_{\parallel} = 13.67$ for *Conf 1*, and $g_{\perp} = 5.6$, $g_{\parallel} = 11.4$ for *Conf 2*. The narrow features marked with an asterisk in Figure 1 arise mostly from the hyperfine interactions with the 23% abundance of ^{167}Er ($I = 7/2$), and some additional trace impurities in the resonator. Since the state of the Er^{3+} ion in this system may be measured by either photoluminescence or EPR, it may be possible to detect the magnetic resonance optically [25].

This interpretation implies that the relative populations of the two configurations of ErSc_2N within the cage change under illumination at 532 nm. The change in spectra shown in Figure 3 is metastable, and persists for many hours after the illumination ceases. The original ‘dark’ spectrum can be recovered by annealing at ~ 30 K. Direct excitation of the Er^{3+} ion at 1496 and 1499 nm has no effect on the EPR spectrum, suggesting that the configuration is affected only by excitation of the fullerene cage or the molecule as a whole, and not by excitation of individual Er^{3+} ions. The magnitude of the effect shows a weak dependence on illumination wavelength in the region < 550 nm (the magnitude of the effect at 550 nm is $\approx 70\%$ that at 400 nm).

In order to deduce the change in populations between *Conf 1* and *Conf 2* from the change in the EPR spectrum under illumination, it is first necessary to relate the EPR intensity to the spin number. This relationship depends on many factors, including transition moment, temperature, microwave power and relaxation times. These terms can be combined into a constant of proportionality κ such that $I_i = \kappa_i N_i$, where I_i represents the intensity of any feature of the spectrum belonging to configuration

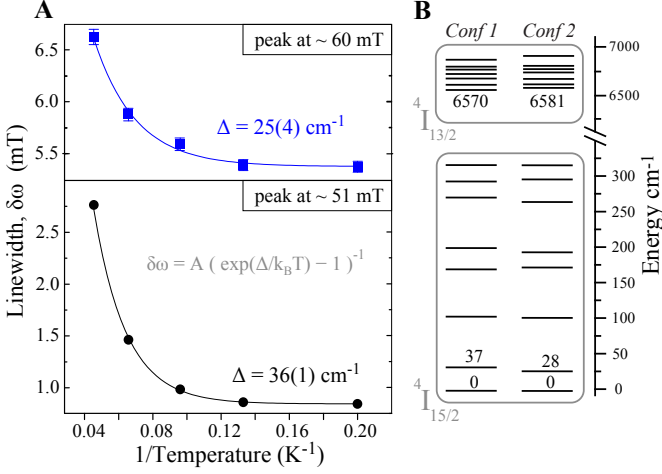


FIG. 2: (A) Linewidth of the two highest intensity features of the CW EPR spectrum shown in Figure 1, at approximately 51 and 60 mT. Their respective energy gaps Δ are obtained under the assumption that the features are homogeneously (lifetime) broadened by an Orbach mechanism (see Eq. 1). These gaps match the energy level diagram (obtained from PL measurements) shown in (B) for the two major configurations of the ErSc_2N rotor inside the cage [11].

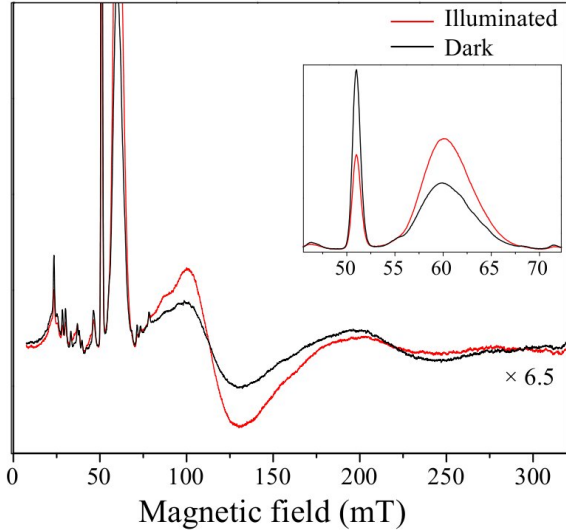


FIG. 3: CW EPR spectra taken at 5 K in the dark, and upon illumination with a 532 nm laser (inset expands the low-field region 45–75 mT). By pairing peaks according to whether their intensities increase or decrease upon illumination, we assign the features centred at approximately 51 and 220 mT to *Conf 1*, and those at 60 and 110 mT to *Conf 2*.

i , and N_i is the number of molecules in configuration i . Then, under the assumption that the total number of spin-active molecules does not change under illumination, the ratio κ_1/κ_2 may be extracted, and thus the fractional occupancy of the two sites before and after illumination. The results are summarised in Table I, which

		I (a.u.)	ΔI	$I/\Delta I$	
51 mT (Site 1)	Dark	1.14	0.53	2.15	
	Light	0.61		1.15	
60 mT (Site 2)	Dark	2.77	-1.71	1.62	
	Light	4.49		2.62	

TABLE I: The integrated areas I of the highest intensity EPR peaks at 51 and 60 mT are compared for spectra taken in the dark and under illumination at 532 nm. Assuming the number of spins contributing to the spectrum remains constant, the change in area ΔI can be used to normalise the peak intensity to produce a value proportional to spin number, and thus extract the occupancy of the two configurations of the ErSc_2N rotor within the fullerene cage. The small (4%) region of each pie chart represents the estimated uncertainty resulting from experimental errors.

examines the dependence of the two sharp features at 51 and 60 mT as a function of illumination.

These results lead us to the remarkable conclusion that illumination turns a slight excess of *Conf 1* into a clear excess of *Conf 2*. It appears the *Conf 1* is marginally favourable in the dark after annealing, but illumination at wavelengths of 532 nm or shorter switches the rotor preferentially to *Conf 2*, where it remains metastable for many hours.

Apparently, illumination at 532 nm generates an excited electronic state (either of the fullerene itself, or by driving charge transfer between the rotor and cage) in which *Conf 2* is substantially favourable. The origin of such a bias is an intriguing question, and may require detailed molecular modeling in order to yield a definitive answer. X-ray diffraction studies have been performed where the $\text{ErSc}_2\text{N}@C_{80}$ is chemically modified to co-crystallise into host [10]. That study revealed two principal configurations of the rotor present across the whole sample which were highly correlated with the two different fullerene orientations arising from different cage functionalisations. It is plausible that the different electronic distributions in these two different cage sites influence the dominant configuration of the internal species. This is consistent with our observation that for pristine cages optical excitation can lead to a switching of the majority species. It is known that the ErSc_2N rotor exhibits an electric dipole moment caused by the differences in electronegativity of erbium and scandium, as evidenced by a high degree of order observed in the XRD study of Ref [10]. Whether illumination creates an exciton on the

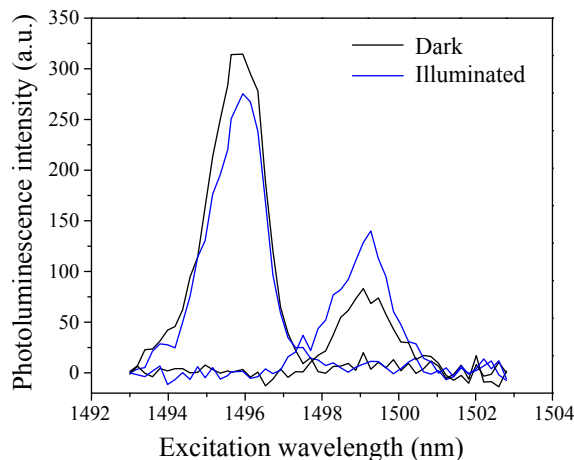


FIG. 4: PLE spectra of $\text{ErSc}_2\text{N}@C_{80}$ in frozen CS_2 solution at 5 K, before (and after) having been illuminated at 532 nm for 20 minutes prior to data acquisition. The peak attributed to *Conf 1* (1496 nm) weakens upon illumination while that attributed to *Conf 2* (1499 nm) increases in intensity, consistent with what is observed in EPR (see Figure 3).

fullerene or drives a charge transfer between the central species and the cage, the electric dipole associated with the cage may assist in producing the observed alignment.

The PLE experiments described in Ref [11] permit the selective excitation of Er^{3+} in the two sites, and could therefore also be used to observe the photoisomerisation described above. Alignment of the optical apparatus was performed with a 532 nm laser beam, as is common practice, at 50 K (i.e. above the configuration annealing temperature of about 30 K found from EPR experiments above). The sample was then cooled down to 5 K and excited with an infra-red laser. For the two configurations, the PLE spectra were acquired while monitoring the fluorescence at respectively 1522 nm (PL peak attributed to *Conf 1*) and 1519 nm (PL peak attributed to *Conf 2*). In the range 1490–1500 nm, PLE peaks were found at 1496 nm for *Conf 1* and 1499 nm for *Conf 2*. 532 nm illumination was then applied for 20 minutes at 5 K and turned off, and a second set of PLE spectra were taken. The results are shown in Figure 4 and unambiguously demonstrate a shift in site occupancy, as observed in EPR, though the noise level in this experiment precludes a quantitative comparison of occupancies.

In summary, the EPR spectrum of $\text{ErSc}_2\text{N}@C_{80}$ reveals two species of Er^{3+} , each with a high degree of apparent axial anisotropy (as expected for the case where the crystal field is much larger than the Zeeman splitting), corresponding to two configurations of the ErSc_2N rotor within the fullerene cage. The relative occupancies of these two orientations can be optically switched, as demonstrated in both EPR and PLE studies. The switching speed and reversibility of this photoisomerisation are yet to be determined; however, the long

lifetime (over 12 hours at 20 K) of the switched orientation may find application in molecular memory elements.

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